

94-333145/41	A14 E14	[SPI. 93.04.02 *WO 9422953-A1 93.04.02 93US-042308 (94.10.13) CO8L 39/06, CO8F 2/10 Prepn. of clear aq. solns. of N-vinylpyrrolidone polymers - uses azobisisobutyronitrile as initiator, gives a high purity prod. while controlling the viscosity (Eng) C94-151580 N(CAJP)R(ATBECHDEDKESFRGBGRIETLUMCNL PT Addnl. Data: MANDELLA W L, THOMAS W, SMITH T E, SHIH J S 94.03.04 94WO-US02345	<p><u>ADVANTAGE</u></p> <p>The use of 2,2'-azobis(2-methylbutanenitrile) produces pure polyvinylpyrrolidone in high yield and avoids objectionable levels of toxic hydrazine and other by products.</p> <p><u>PREFERRED PROCESS</u></p> <p>The wt. ratio of initiator to N-vinylpyrrolidone reactant is between 0.00005:1 and 0.1:1.</p> <p>The polymerisation reaction is carried out with the aid of a buffering agent in a conc. of 0.1-2 wt. % of the total reaction mixt.</p> <p>The wt. ratio of N-vinylpyrrolidone reactant to water is 1:1 to 1:2 and the polymerised product has a K-value above 100. When the wt. ratio of N-vinylpyrrolidone reactant to water is 1:3-1:4 the polymerised prod. has a K-value of less than 100.</p> <p>The polymerisation reaction is carried out at a pH of 6-11. At least a portion of the initiator soln. in step (a) is charged to the reactor during the polymerisation reaction.</p> <p>At least a portion of the N-vinylpyrrolidone reactant in (b) is gradually fed to the reactor during the course of polymerisation.</p>	WO9422953-A+
		The prepn. of an N-vinylpyrrolidone polymer as a clear aq. soln. comprises (a) preparing a 5-75 wt. % soln. or emulsion of 2,2'-azobis(2-methyl butanenitrile) initiator in N-vinylpyrrolidone solvent, a water soluble oligomer of N-vinyl pyrrolidone solvent or an aq. soln. of the solvents; (b) separately dissolving N-vinylpyrrolidone monomer or oligomer reactant, contg. a minor amt. of a polymerisable vinyl comonomer, in water, in a wt. ratio of between 1:1 and 1:5 based on total monomer and/or oligomer; and (c) contacting soln. (a) and soln. (b) in a reaction at 60°C-105°C at or about atmospheric pressure with constant agitation until a clear N-vinylpyrrolidone polymer aq. soln. contg. less than 0.1 wt. % monomer is obtainable.		

The polymerisation temp. is raised 3-20°C after the unreacted monomer level in the reaction is 10 wt. % or less. The polymerisation temp. is 60-75°C to obtain a polymeric prod. having a K-value above 100. The polymerisation temp. to 80-105°C to obtain a polymeric product having a K-value less than 100. At least a portion of (a) is added to the reactor after the temp. is raised and after the unreacted monomer level falls below 6%.

EXAMPLE

Into a reactor contg. a thoroughly mixed buffer soln. contg. 392.2 ml dionised water and 1.3 g tetrasodium pyrophosphate was introduced N<sub>2</sub> gas at a rate of 1.5 l/min and the purge was maintained throughout the reaction. Vinylpyrrolidone (17.87 g) was charged to the reactor, heated to 70°C and 0.6 g 2,2'-azobis(2-methylbutanenitrile) initiator predissolved in 1 g N-vinylpyrrolidone solvent was then added.

The mixt. was agitated and reacted for 4 hrs at 70°C until the vinylpyrrolidone monomer level was below 6%, after which an additional 0.3 g initiator in 0.5 g vinylpyrrolidone and 35.25 g deionised water was charged at a rate of 15 ml per min over 3 hrs. After 1.5 hrs of water introduction, a further charge of 0.3 g initiator in 0.5 g vinylpyrrolidone was introduced to the continuously agitated contents of the

reactor. Upon completion of the water addition, the reaction mixture was heated to 75°C and held at that temp. for 60 mins to complete the polymerisation of N-vinylpyrrolidone to N-vinylpyrrolidone homopolymer which was recovered as a uniformly clear, aq. soln. contg. less than 0.1% unreacted monomer.

The homopolymer had a K-value of 120 and was recovered in 99.9% yield. (17pp2156 DwgNo 0/0).

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(54) Title: PREPARATION OF CLEAR SOLUTIONS OF N-VINYLPYRROLIDONE POLYMERS

(57) Abstract

This invention relates to a process for the preparation of clear, aqueous solutions of N-vinylpyrrolidone polymers in high purity by contacting a vinylpyrrolidone solution of 2,2'-azobis(2-methyl-butanenitrile) initiator with vinylpyrrolidone monomer or a water soluble polymerizable vinylpyrrolidone oligomer and simultaneously controlling the polymer product viscosity to a predetermined K-value of between about 15 to about 130 by adjustment of one or more of several process options.

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## PREPARATION OF CLEAR SOLUTIONS OF N-VINYLPYRROLIDONE POLYMERS

In one aspect the invention relates to the production of an aqueous, clear solution of pure N-vinylpyrrolidone polymer under mild reaction conditions and in another aspect, the invention relates to the process for the preparation of clear polyvinylpyrrolidone aqueous solutions having a predetermined K-value. In still another aspect, the invention relates to a process for the preparation of a water soluble polyvinylpyrrolidone having a K-value of up to 130 in aqueous solution.

BACKGROUND OF THE INVENTION

Various methods have been proposed for the polymerization of vinylpyrrolidone (VP) including the polymerization in an aqueous solution of hydrogen peroxide initiator with the addition of ammonia to regulate the pH. However, in this process, only low to moderately high molecular weights are obtained and undesirable by-products can be formed. When ammonia is replaced with potassium hydroxide, by-product generation is reduced; although other contaminating inorganic components, including ash, are present which cause cloudiness when employed with organic solvents (German Patent Application No. 3532747.2). Also, very high molecular weight polymers are difficult to obtain. It has also been suggested (EPA 104,042) that polymerization be effected using tertiary-butyl peroxyvalate as an initiator. However, this procedure does not provide polymers which dissolve in water to form clear solutions.

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Another process using di-tertiary-butyl peroxide initiator to polymerize vinylpyrrolidone in aqueous solution (U.S. Patent 4,816,534) has many drawbacks including the inability to form polymer of K value above 80 and the need for an organic solvent which resists complete removal from the product. Also, the synthesis with di-t-butyl peroxide requires relatively severe conditions of temperature and pressure. Addition of molecular weight regulators, such as isopropanol, mercaptans and other thio compounds is objectionable since they require steam distillation for their removal. Because of lengthy process steps involving incorporation of organic solvent and controls on temperature and pressure, these processes are both expensive and time consuming, hence they do not offer a practical solution to achievement of the desired goal, namely, the production of a clear solution of substantially pure vinylpyrrolidone polymer.

Accordingly, it is an object of this invention to provide a commercially feasible and economically simplified process for the preparation of clear, aqueous solutions of vinylpyrrolidone polymer.

Another object of this invention is to produce a clear, aqueous solution of vinylpyrrolidone polymer having a Fikentscher K-value of up to 130.

Still another object is to provide a process which operates under mild conditions to produce a vinylpyrrolidone polymer of predetermined 15-130 K-value containing substantially no harmful contamination.

These and other objects of the invention will become apparent from the following description and disclosure.

THE INVENTION

In accordance with this invention there is provided a process for producing a N-vinylpyrrolidone polymer of predetermined Fikentscher K-value as a clear, aqueous solution which comprises contacting N-vinylpyrrolidone monomer, or a polymerizable water soluble oligomer thereof, in aqueous solution with a solution or microemulsion of 2,2'-azobis(2-methylbutane-nitrile) initiator dissolved or emulsified in (1) N-vinylpyrrolidone solvent, (2) a mixture of the vinylpyrrolidone and water or (3) water-soluble poly(N-vinylpyrrolidone), to polymerize said monomer, which polymerization reaction is optionally carried out in the presence of a buffer solution.

The vinylpyrrolidone monomers or polymerizable oligomers of this invention include N-vinylpyrrolidone alone or mixtures of these, optionally containing a minor amount, usually less than 35 wt. %, of polymerizable vinyl comonomers such as a vinyl ester, an acrylate, N-vinyl caprolactam or methacrylate and acrylamide or methacrylamide. However, the preferred reactant in the present process is the N-vinyl-2-pyrrolidone monomer and the preferred product is the homopolymer of N-vinyl-pyrrolidone. The vinylpyrrolidone monomer, oligomer or monomer-oligomer or comonomer mixture is polymerized in aqueous solution wherein the weight ratio of total monomer and/or oligomer to deionized water is between about 1:1 and about 1:5, depending upon the predetermined K-value of the polymer product to be achieved. Generally, it is found that higher concentrations of water, e.g. wt. ratio of 1:3, in the reactor lead to lower product K-values.

20-50%

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The reaction mixture may also contain a buffer to prevent hydrolysis of the monomer in the event that the pH falls below 6. Representative pH levels during the reaction are 6 to 11; however a pH above 7 is most desired. Suitable buffers include sodium bicarbonate, tetrasodium pyrophosphate, ammonia, etc. The buffer, when used, is generally employed as an aqueous solution containing from about 0.01 to 2 wt. % buffer.

Although the 2,2'-azobis(2-methylbutanenitrile) initiator can be charged to the reactor as a solid it is preferably employed as a 5 to 75 wt. % solution or emulsion, preferably a 20 to 65 wt. % solution or emulsion, of initiator in N-vinylpyrrolidone solvent. It has been found that addition of initiator in solid form may not provide intimate contact with the reactant species in the initial stages of the polymerization and that the concentration of initiator at various stages of the polymerization is more difficult to control. The manner of introducing the initiator solution can be carried out in several ways. For example, the total initiator charge can be introduced before polymerization takes place or the initiator can be added gradually or in increments at intervals over a period of from about 6 to about 20 hours, more often from about 8 to about 12 hours, during the course of the reaction until the unreacted monomer level is 0.1% or less.

Generally the weight ratio of initiator to total monomer or oligomer reactant feed to the reactor is between about 0.00005:1-0.1:1, preferably between about 0.0003:1-0.01:1.

The polymerization is conducted in an oxygen free atmosphere under mild conditions at a temperature of from about 50° to about 105°C., preferably from about 60° to about 101°C., at or about atmospheric pressure. The oxygen free atmosphere can be maintained with a constant nitrogen purge throughout the reaction.

As indicated above, the versatility of the present process provides methods for controlling the K-value of the polymerized product produced to meet predetermined specifications. This can be accomplished by adjustment of any one or more of several operating parameters. More specifically, to achieve higher K-values, a more concentrated solution of monomer or oligomer in the initial aqueous solution can be employed, a reaction temperature within the lower portion of the above range can be used for the reaction, introduction of at least a major portion of the total reaction initiator charge at the beginning of the polymerization can be applied or any combination of the above procedures. Lower K-values are achieved by the converse of the above measures or by introducing a small amount of concentrated monomer or oligomer toward the end of the reaction after about 90% of the polymerization is achieved. The viscosity of the polymer can be evaluated during polymerization by taking aliquot samples and making the indicated adjustments in the system to meet the desired K-value.

Also as indicated above, the present polymerization reaction can be carried out by initially charging deionized water, vinylpyrrolidone monomer or oligomer in desired concentration and optionally a buffer solution to the reactor and thereafter mixing with the initiator solution which is added initially in total amount or added gradually or in precise increments throughout the reaction. Alternatively, the monomer or oligomer solution can be added gradually throughout the course of the reaction to a predissolved or pre-emulsified initiator solution, however, the gradual introduction of initiator solution throughout the reaction is generally preferred.

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Additionally, the temperature of the reaction can be varied after a major portion of monomer has been converted to polymer. For example, when unreacted monomer is about 10% or less, the reaction temperature can be raised 3-20°C. to complete the polymerization to achieve a higher K-value, when such is desired. However, polymerizations carried out at the same temperature or a later adjusted lower temperature, depending on desired K-value, can also be employed.

As indicated above, the present process shows many advantages over those of the prior art, in that the use of 2,2'-azobis(2-methylbutanenitrile) produces pure polyvinylpyrrolidone in high yield and avoids objectionable levels of toxic hydrazine and other by-products. The present process is carried out under relatively mild conditions of temperature and pressure and presents several means for controlling the K-value of the polymeric product to a predetermined limit by adjustment of the lactam concentration in the aqueous feed, by regulation of the overall reaction temperature or the temperature at the final stages of polymerization, by control of the amount of initiator introduced at the beginning of the polymerization and by supplemental introduction of monomer at a later stage in the polymerization process. The above regulatory measures are economically effected without the addition of contaminating excipients. Finally, pure, dry polyvinylpyrrolidone product can be recovered from solution by evaporation of water and ground to any particle size, if desired.

Having thus described the invention, reference is now had to the following examples which illustrate preferred embodiments but which are not to be construed as limiting to the scope of the invention more broadly described above and in the appended claims.

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EXAMPLE 1

Into a 20 liter jacketed reactor equipped with a nitrogen inlet valve and containing a thoroughly mixed buffer solution of 3922 ml of deionized water and 1.3 grams of tetrasodium pyrophosphate, was introduced nitrogen gas at a rate of 1.5 liters/minute which purge was maintained throughout the ensuing reaction.

Vinylpyrrolidone (1787 grams) was then charged to the reactor, heated to 70°C., followed by 0.6 grams of 2,2'-azobis(2-methylbutanenitrile) initiator predissolved in 1 gram of N-vinylpyrrolidone solvent. The resulting mixture was agitated and reacted for 4 hours at 70°C. until the vinylpyrrolidone (VP) monomer level was below 6%, after which an additional 0.3 grams of initiator in 0.5 grams of vinylpyrrolidone and 3525 grams of deionized water was charged at a rate of 15 ml per minute over an additional 3 hour period. After 1.5 hours of water introduction, a further charge of 0.3 grams of initiator in 0.5 grams of vinylpyrrolidone was introduced to the continuously agitated contents of the reactor. Upon completion of water addition, the reaction mixture was heated to 75°C. and held at that temperature for about 60 minutes to complete the polymerization of N-vinylpyrrolidone to N-vinylpyrrolidone homopolymer which was recovered as a uniformly clear, aqueous solution, containing less than 0.1% unreacted monomer. The homopolymer had a K-value of 120 and was recovered in 99.9% yield.

EXAMPLE 2

Into a 20 liter jacketed reactor, equipped with a double turbine stirrer, thermocouples, reflux condenser, nitrogen inlets at the top and bottom of the reactor and a rpm/torque monitor, was charged 3922 grams of deionized water and 1.3 grams of tetrasodium pyrophosphate buffer (TSPP). This mixture was stirred for about 8 minutes at 150 rpm until a solution was formed. A nitrogen purge at a rate of 1.5 liters/minute entering the system from the bottom of the reactor was maintained throughout the reaction. N-vinylpyrrolidone (1787 grams) was then added and the reactor contents heated to 70°C. After about 5 minutes, a solution of 0.6 grams of 2,2'-azobis(2-methylbutanenitrile) initiator dissolved in 2.0 grams of N-vinylpyrrolidone was gradually added to the system over a period of about 3.5 hours and mixed until the monomer concentration dropped below 6%, whereupon additional initiator solution (0.3 grams initiator dissolved in 0.5 grams of N-vinylpyrrolidone) was added. Deionized water (3525 grams) was then charged over a period of 3 hours and after about 1.5 hours of water addition, another 0.3 grams of initiator dissolved in 0.5 grams of N-vinylpyrrolidone was added. After 3 hours had elapsed the reaction mixture was heated to 75°C. and held at that temperature for an additional 3 hours during which 2 additional charges of 0.3 grams initiator dissolved in 0.5 grams of N-vinylpyrrolidone were introduced to complete the polymerization. The product was cooled to room temperature and was found to have a monomer concentration of less than 0.02%, a K-value of 126.5 (0.1% solution in water) was recovered as a clear aqueous solution containing 19.2 wt. % of N-vinylpyrrolidone homopolymer.

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EXAMPLE 3

The same apparatus and general procedure as described in Example 1 was employed in this example. The reactor was purged with nitrogen and 3,000 grams of deionized water, 1,300 grams of N-vinylpyrrolidone, 4.6 grams of concentrated ammonium hydroxide and 0.45 grams of ethylenediamine tetraacetic acid (EDTA) was charged. The mixture was agitated at 250 rpm and the nitrogen purge was continued throughout the reaction. The reaction mixture was heated to 78-80°C. and maintained at this temperature throughout most of the reaction. At this temperature, 1.8 grams of ABMB, i.e. 2,2'-azobis(2-methylbutanenitrile) dissolved in 3 grams of N-vinylpyrrolidone was charged, after which a solution of 6800 grams of deionized water and 2900 grams of vinylpyrrolidone was pumped into the reactor over a period of 3 hours.

Additional charges of 0.6 grams of ABMB dissolved in 2.4 grams of N-vinylpyrrolidone were then added every 30 minutes for a total of 6 charges. Finally, two additional charges totalling 3.1 grams initiator in N-vinylpyrrolidone were introduced after the monomer content level fell below 6%. The reaction mixture was cooled to room temperature and was recovered as a clear, aqueous solution containing 30.1% N-vinylpyrrolidone homopolymer having a K-value (1% solution in water) of 94.5 and a monomer content of 0.08%.

EXAMPLE 4

The same apparatus and general procedure as described in Example 1 was used for this example. The reactor was purged with nitrogen and 3,077 grams of deionized water, 833 grams of N-vinylpyrrolidone, 4.6 grams of concentrated ammonium hydroxide and 0.45 grams

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of ethylene diamine tetraacetic acid was charged. The mixture was agitated at 250 rpm under a nitrogen blanket. The reaction mixture was heated to 80-82°C. and maintained at this temperature throughout most of the reaction. After about 5 minutes, 4.5 grams of initiator dissolved in 3 grams of N-vinylpyrrolidone was charged, and after 30 minutes, a solution of 7535 grams of deionized water and 2497 grams of vinylpyrrolidone was gradually pumped into the reactor over a period of 4 hours. Additional charges of 1.47 grams of initiator dissolved in 1.53 grams of N-vinylpyrrolidone were added every 60 minutes for a total of 6 charges.

After 60 minutes of water/vinylpyrrolidone addition, the temperature was gradually raised to 85°C. and after 1 hour agitation at this temperature the homopolymerization was completed. The reaction mixture was cooled to room temperature and was recovered as a clear, aqueous solution containing 24.3% N-vinylpyrrolidone homopolymer having a K-value (1% solution in water) of 74.8 and a monomer content of 0.06%.

#### EXAMPLE 5

The same apparatus and general procedure outlined in Example 1 was used in this example. The reactor was purged with nitrogen and 6,845 grams of deionized water, 833 grams of N-vinylpyrrolidone, 4.6 grams of concentrated ammonium hydroxide and 0.46 grams of EDTA was charged. The mixture was agitated at 250 rpm and the nitrogen purge was continued throughout the reaction. The reaction mixture was heated to 94°C. and maintained at this temperature during the addition of 4.5 grams of 2,2'-azobis(2-methylbutanenitrile) initiator dissolved in 8 grams of N-vinylpyrrolidone after which

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the temperature rose to 101°C. and was thereafter maintained at 99-101°C. After 30 minutes, a solution of 3767 grams of deionized water and 2497 grams of vinylpyrrolidone was pumped into the reactor over a period of 4.5 hours. Additional charges of 1.47 grams of initiator dissolved in 1.53 grams of N-vinylpyrrolidone were made every 30 minutes after beginning the water/vinylpyrrolidone feed for a total of 6 charges. Two additional charges of initiator totalling 3.0 grams initiator were introduced after the monomer content level fell below 6%. The reaction mixture was then cooled to room temperature and polyvinylpyrrolidone was recovered as a clear, aqueous solution containing 23.9% N-vinylpyrrolidone homopolymer having a K-value (1% solution in water) of 61.1 and a monomer content of 0.07%.

EXAMPLES 6-9

The same apparatus and general procedure as employed in Example 1 was used, except that the weight ratios of total initiator to vinylpyrrolidone solvent, total initiator to vinylpyrrolidone reactant and total water to vinylpyrrolidone were varied as shown in the following Table to achieve the predetermined K-values reported therein.

TABLE

<u>Example</u>	<u>K-value</u>	<u>Total Initiator to H<sub>2</sub>O ratio (wt/wt)</u>	<u>Buffer to Water ratio (wt/wt)</u>	<u>Total Initiator to VP reactant ratio (wt/wt)</u>	<u>Total Water to VP in System ratio (wt/wt)</u>
6	130	1.8/7447	1.3/7447	1.8/1790	7447/1790
7	90	8.5/9883	4.6/9883	8.5/4217	9803/4217
8	75	13.3/10615	4.6/10615	13.3/3342	10615/3342
9	60	16.3/10615	4.6/10615	16.3/3351	10615/3351

In each case the polyvinylpyrrolidone was recovered as a clear aqueous solution containing less than 0.1% unreacted monomer.

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EXAMPLE 10

When Example 1 is repeated with 2,2'-azobis-(methylpropanenitrile) substituted for 2,2'-azobis-(methylbutanenitrile) initiator a portion of the initiator decomposes to form toxic tetramethyl succinonitrile in the system.

EXAMPLE 11

Example 1, repeated with 2,2'-azobis-(2,4-dimethylpentanenitrile) substituted for 2,2'-azobis-(2-methylbutanenitrile), results in a cloudy product due to the increased insolubility of this initiator.

## WHAT IS CLAIMED IS:

1. The process of producing an N-vinylpyrrolidone polymer as a clear aqueous solution which comprises:

(a) preparing a 5 to 75 wt. % solution or emulsion of 2,2'-azobis(2-methylbutanenitrile) initiator in N-vinylpyrrolidone solvent, a water-soluble oligomer of N-vinyl pyrrolidone solvent or an aqueous solution of said solvents;

(b) separately dissolving N-vinylpyrrolidone monomer or oligomer reactant, optionally containing a minor amount of a polymerizable vinyl comonomer, in water in a weight ratio of between about 1:1 and about 1:5 based on total monomer and/or oligomer and

(c) contacting solution (a) and solution (b) in a reactor at a temperature of from about 60°C. to about 105°C., at or about atmospheric pressure with constant agitation until a clear N-vinylpyrrolidone polymer aqueous solution containing less than 0.1 wt. % monomer is obtained.

2. The process of claim 1 wherein the weight ratio of initiator to N-vinylpyrrolidone reactant is between about 0.00005:1 and about 0.1:1.

3. The process of claim 1 wherein the polymerization reaction is carried out at a pH of from about 6 to 11.

4. The process of claim 1 wherein the polymerization reaction is carried out with the aid of a buffering agent in a concentration of from about 0.01 to about 2 wt. % of the total reaction mixture.

5. The process of claim 1 wherein the weight ratio of N-vinylpyrrolidone reactant to water is between about 1:1 and about 1:2 and the polymerized product has a K-value above 100.

6. The process of claim 1 wherein the weight ratio of N-vinylpyrrolidone reactant to water is between about 1:3 and about 1:4 the polymerized product has a K-value of less than 100.

7. The process of claim 1 wherein at least a portion of the initiator solution in step (a) is charged to the reactor during the polymerization reaction.

8. The process of claim 7 wherein at least a portion of the N-vinylpyrrolidone reactant in step (b) is gradually fed to the reactor during the course of polymerization.

9. The process of claim 1 wherein the polymerization temperature is raised 3-20°C. after the unreacted monomer level in the reaction is about 10 wt. % or less.

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10. The process of claim 1 wherein the polymerization temperature is between about 60 and about 75°C. to obtain a polymeric product having a K-value above 100.

11. The process of claim 1 wherein the polymerization temperature is between about 80° and about 105°C. to obtain a polymeric product having a K-value less than 100.

12. The process of claim 1 wherein at least a portion of (a) is added to the reactor after the unreacted monomer level falls below 10%.

13. The process of claim 9 wherein at least a portion of (a) is added to the reactor after the temperature is raised.

14. The process of claim 9, 12 or 13 wherein the portion of (a) is added to the reactor after the unreacted monomer level falls below 6%.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/02345

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08L 39/06; C08F 2/10

US CL :524/808; 526/219.5

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/808; 526/219.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category <sup>a</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 1,021,121 (GENERAL ANILINE & FILM CORPORATION) 23 FEBRUARY 1966; Page 2 right column lines 43-44; Examples 2 and 4.	1-14
Y	US, A, 4,554,312 (BARABAS ET AL.) 19 NOVEMBER 1985; Abstract.	1-14
Y	US, A, 4,330,451 (STRAUB ET AL.) 18 MAY 1982; Abstract.	1-14

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search

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